(12) UK Patent Application (19) GB (11) 2 371 551 (13) A

(43) Date of A Publication 31.07.2002

(21) Application No 0102227.6

(22) Date of Filing 29.01.2001

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(51) INT CL[7]
C09D 11/10 11/00

(52) UK CL (Edition T)
C3V VAM
C3W W224 W302
U1S S1390 S2248

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(58) Field of Search
UK CL (Edition S) C3P PFE , C3V VAL VAM
INT CL[7] C09D 11/00 11/10
Online: WPI, EPODOC, JAPIO

(54) Abstract Title
A Printing Ink

(57) Inks are disclosed which are useful in ink-jet printing. The inks are cured by ultraviolet radiation, preferably free radical radiation. The inks contain a multifunctional acrylate monomer, a vinyl ether monomer and a photoinitiator. After curing, the inks desirably exhibit low viscosity and give tough printed images.

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A Printing Ink

This invention concerns inks for use in ink-jet printers. In particular, this invention concerns inks for use in ink-jet printers that are cured using ultraviolet radiation.

In ink-jet printing, minute droplets of black or coloured ink are ejected in a controlled manner from one or more reservoirs or printing heads through narrow nozzles on to a substrate which is moving relative to the reservoirs. The ejected ink forms an image on the substrate. For high-speed printing, the inks must flow rapidly from the printing heads, and, to ensure that this happens, they must have in use a low viscosity, typically below 50 mPa.s at 25ºC and in many applications below 25 mPa.s. Typically, when ejected through the nozzles, the ink has a viscosity of 10.5 mPa.s at 25ºC (the ink might have a much higher viscosity at ambient temperature). The inks must also be resistant to drying or crusting in the reservoirs or nozzles. For these reasons, ink-jet inks for application at or near ambient temperatures are commonly formulated to contain a large proportion of a mobile liquid vehicle or solvent. In one common type of ink-jet ink this liquid is water - see for example the paper by Henry R. Kang in the Journal of Imaging Science, 35(3), pp. 179-188 (1991). In those systems, great effort must be made to ensure the inks do not dry in the head due to water evaporation. In another common type the liquid is a low-boiling solvent or mixture of solvents - see, for example, EP 0 314 403, EP 0 424 714 and GB9927247.8. Unfortunately, ink-jet inks that include a large proportion of water or solvent cannot be handled after printing until the inks have dried, either by evaporation of the solvent or its absorption into the substrate. This drying process is often slow and in many cases (for example, when printing on to a heat-sensitive substrate such as paper) cannot be accelerated.

Another type of ink-jet ink contains unsaturated organic compounds, termed monomers, which polymerise by irradiation, commonly with ultraviolet light, in the presence of a photoinitiator. This type of ink has the advantage that it is not necessary to evaporate the liquid phase to dry the print; instead the print is exposed to radiation to cure or harden it, a process which is more rapid than evaporation of solvent at moderate temperatures. These monomers may be acrylate or

methacrylate esters, as is disclosed in EP 0540203B, US-A-5,270,368 and in WO 97 31071. In such inks it is necessary to use monomers possessing a low viscosity. In practice it is difficult to find acrylate monomers or combinations of acrylate monomers which do not give compositions with an unacceptably high viscosity for ink-jet printing. This is especially true if materials are selected with more than one polymerisable functional group in the molecule, though these monomers have the advantage of giving a more cross-linked, and therefore tougher, polymer after irradiation. Likewise materials of higher molecular weight usually, other things being equal, give after polymerisation more resistant films, but compositions using them are more viscous. In practise monofunctional acrylate monomers need to be used with multifunctional acrylate monomers to arrive at a suitably low viscosity for ink-jet printing. However, this tends to reduce the cure speed and affects such properties as adhesion and toughness.

Other known low viscosity photopolymerisable monomers have been used in ink-jet inks e.g. vinyl ethers, as disclosed in EP779346. In this case the vinyl ether is used as a cationic photopolymerisable monomer. However, cationic curing tends to be slow compared with radical systems.

We have discovered that using vinyl ethers as photopolymerisable monomers in radical systems achieves low viscosity inks suitable for ink-jet printing without the need for monofunctional acrylate monomers. These systems also give acceptable end-user properties such as good cure, adhesion and chemical resistance.

An aim of the present invention is to provide an ink that is cured by ultraviolet irradiation and is suitable for application by ink-jet printing.

A further aim of the present invention is to provide an ink which does not contain water or volatile organic solvents.

A further aim of the present invention is to provide an ink that does not contain monofunctional monomers.

In accordance with the present invention, there is provided an ink jet ink including at least one multifunctional acrylate monomer, at least one vinyl ether monomer, and at least one photoinitiator.

We have found that this ink jet ink unexpectedly exhibits a desirable low viscosity (preferably less than 100 mPas, more preferably less than 50 mPa.s and most preferably less than 25 mPas at 25ºC) so that the use of monofunctional acrylate monomers is unnecessary. The ink is therefore preferably substantially free from monofunctional monomers. By 'substantially free', we mean that no monofunctional monomers need to be deliberately added to the ink; however, the ink may include insignificant traces of monofunctional monomers which are only present in the ink by way of impurity from other components. The preferred ratio by weight is from 5 to 15 parts of multifunctional acrylate monomer to 1 part of vinyl ether monomer.

Typical multifunctional acrylate monomers useful in our compositions are hexanediol diacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, polyethyleneglycol diacrylate, neopentylglycol diacrylate, and the acrylate esters of ethoxylated or propoxylated glycols and polyols, for example propoxylated neopentyl glycol diacrylate and ethoxylated trimethylolpropane triacrylate. Preferred are difunctional acrylates with a molecular weight greater than 200. Mixtures of acrylates may be used. The proportion of multifunctional acrylate monomer is between 50 and 95% by weight, preferably between 60 and 80%.

Typical vinyl ether monomers useful in our invention are triethylene glycol divinyl ether, diethylene glycol divinyl ether, 1,4- cyclohexanedimethanol divinyl ether and ethylene glycol monovinyl ether. Mixtures of vinyl ether monomers may be used. The proportion of multifunctional vinyl ether monomer is preferably between 1 and 20% by weight, more preferably between 7 and 15%, provided that the ratio of acrylate monomer to vinyl ether monomer lies between 5:1 and 15:1. Preferably multifunctional, more preferably difunctional and trifunctional vinyl ether monomers are used.

In addition to the monomers described above, the compositions include a photoinitiator, which, under irradiation by ultraviolet light, initiates the polymerization of the monomers. Preferred are photoinitiators which produce free radicals on irradiation (free radical photoinitiators) such as, for example, benzophenone, 1-hydroxycyclohexyl phenyl ketone, 2-benzyl-2-dimethylamino-(4-morpholinophenyl)butan-1-one, benzil dimethylketal, bis(2,6-dimethylbenzoyl)-2,4,4-trimethylpentylphosphine oxide or a mixture thereof. Such photoinitiators are known and commercially available such as, for example, under the trade names Irgacure, Darocur (from Ciba) and Lucerin (from BASF). The proportion of photoinitiator preferably lies between 1 and 20% by weight, more preferably between 4 and 10% by weight.

The ink-jet ink of the present invention also includes a colouring agent, which may be either dissolved or dispersed in the liquid medium of the ink. Preferably the colouring agent is a dispersible pigment, of the types known in the art and commercially available such as, for example, under the trade-names Paliotol (available from BASF plc), Cinquasia, Irgalite (both available from Ciba Speciality Chemicals) and Hostaperm (available from Clariant UK). The pigment may be of any desired colour such as, for example, Pigment Yellow 13, Pigment Yellow 83, Pigment Red 9, Pigment Red 184, Pigment Blue 15:3, Pigment Green 7, Pigment Violet 19, Pigment Black 7. Especially useful are black and the colours required for trichromatic process printing. Mixtures of pigments may be used. The total proportion of pigment present is preferably between 0.5 and 12% by weight, more preferably 1 - 5% by weight.

Other components of types known in the art may be present in the ink to improve the properties or performance. These components may be, for example, surfactants, defoamers, dispersants, synergists for the photoinitiator, stabilisers against deterioration by heat or light, reodorants, flow or slip aids, biocides and identifying tracers.

The inks of the invention may be prepared by known methods such as, for example, stirring with a high-speed water-cooled stirrer, or milling on a horizontal

bead-mill.

The invention will now be described, by way of example, with reference to the following examples (parts given are by weight):

EXAMPLE 1 - Magenta UV Ink-jet Ink

The following components were mixed in the order given on a high-speed water-cooled stirrer:

Propoxylated neopentylglycol diacrylate	69.82 parts
Actilane 505 (wetting resin from Akcros)	1.56 parts
Solsperse 32000 (dispersant from Avecia)	1.25 parts
Hostaperm E5BO2 (pigment from Hoechst)	3.60 parts
Genorad 16 (stabiliser from Rahn AG)	0.12 parts
Rapi-cure DVE-3 (difunctional vinyl ether from ISP Europe)	10.0 parts
Lucirin TPO (photoinitiator from BASF)	8.6 parts
Benzophenone (photoinitiator)	5.0 parts
Byk 307 (defoamer from BYK Chemie)	0.05 parts

The product was an ink having a viscosity of 22 mPas at 25ºC. The ink was printed on to self-adhesive vinyl and irradiated by passing at 40 m/min under light from an iron-doped ultra-violet lamp of power 120 W/cm. The ink gave a print with good cure, adhesion and chemical resistance.

EXAMPLE 2 - Cyan UV Ink-jet Ink

The following components were mixed in the order given on a high-speed water-cooled stirrer:

Hexanediol diacrylate		1.93 parts
Actilane 505	(wetting resin from Akcros)	0.67 parts
Solsperse 32000	(dispersant from Avecia)	0.45 parts

Solsperse 5000 (dispersant from Avecia)	0.05 parts
Genorad 16	0.05 parts
Irgalite Blue GLVO (blue pigment from Ciba)	1.35 parts
Propoxylated neopentylglycol diacrylate	75 parts
Rapi-cure DVE-3 (difunctional vinyl ether from ISP Europe)	10 parts
Lucirin TPO (photoinitiator from BASF)	8.0 parts
Benzophenone (photoinitiator)	2.0 parts
Byk 307 (defoamer from BYK Chemie)	0.5 parts

The product was an ink having a viscosity of 18.4 mPas at 25ºC. The ink was printed on to self-adhesive vinyl and exposed by passing at 40 m/min under light from an iron-doped ultraviolet lamp of power 120 W/cm. As in Example 1 the ink gave a print with good cure, adhesion and chemical resistance.

CLAIMS

1. A printing ink including at least one multifunctional acrylate monomer, at least one vinyl ether monomer and at least one photoinitiator.

2. The ink claimed in claim 1, wherein the ink is substantially free from monofunctional acrylate monomers.

3. The ink claimed in claims 1 or 2, wherein the ink includes, by weight, from 5 to 15 parts of multifunctional acrylate monomer to 1 part of vinyl ether monomer.

4. The ink claimed in any one of the preceding claims, wherein the multifunctional acrylate monomer is selected from: hexanediol diacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, polyethyleneglycol diacrylate, neopentylglycol diacrylate; acrylate esters of ethoxylated or propoxylated glycols and polyols, preferably propoxylated neopentyl glycol diacrylate and ethoxylated trimethylolpropane triacrylate; difunctional acrylates with a molecular weight greater than 200; and mixtures thereof.

5. The ink claimed in any one of the preceding claims, wherein the multifunctional acrylate monomer is present in an amount from 50 to 95% by weight, preferably from 60 to 80% by weight.

6. The ink claimed in any one of the preceding claims, wherein the vinyl ether monomer is selected from : diethylene glycol divinyl ether, 1,4-cyclohexanedimethanol divinyl ether, triethylene glycol divinyl ether, ethylene glycol monovinyl ether and 1,4- cyclohexanedimethanol divinyl ether.

7. The ink claimed in any one of the preceding claims, wherein the vinyl ether monomer is present from 1 to 20% by weight, preferably from 7 to 15%, provided that the ratio of multifunctional acrylate monomer to vinyl ether monomer lies between 5:1 and 15:1.

8. The ink claimed in any one of the preceding claims, wherein the photoinitiator is a free radical photoinitiator, preferably selected from: benzophenone, 1-hydroxycyclohexyl phenyl ketone, 2-benzyl-2-dimethylamino-(4-morpholinophenyl)butan-1-one, benzil dimethylketal, bis(2,6-dimethylbenzoyl)-2,4,4-trimethylpentylphosphine oxide or a mixture thereof.

9. The ink claimed in any one of the preceding claims, wherein the photoinitiator is present from 1 to 20% by weight, preferably from 4 to 10% by weight, of the ink.

10. The ink claimed in any one of the preceding claims, wherein the ink includes a dispersible pigment as a colouring agent.

11. The ink claimed in claim 10, wherein the dispersible pigment is present from 0.5 to 12% by weight, more preferably from 1 to 5% by weight, of the ink.

12. The ink claimed in any one of the preceding claims, wherein the printing ink is an ink jet ink.

13. A method of printing, wherein the method uses the ink claimed in any one of claims 1-11.

14. A method of ink jet printing, wherein the method uses the ink claimed in claim 12.

Amendments to the claims have been filed as follows

1. An ink-jet ink which is substantially free of water or volatile organic solvents, including at least one multifunctional acrylate monomer, at least one vinyl ether monomer, at least one photoinitiator and at least one colouring agent, the ink having a viscosity of less than 100 mPas.

2. The ink claimed in claim 1, wherein the ink is substantially free from monofunctional acrylate monomers.

3. The ink claimed in claims 1or 2, wherein the ink includes, by weight, from 5 to 15 parts of multifunctional acrylate monomer to 1 part of vinyl ether monomer.

4. The ink claimed in any one of the preceding claims, wherein the multifunctional acrylate monomer is selected from: hexanediol diacrylate, trimethylolpropane triacrylae, pentaerythritol triacrylate, polyethyleneglycol diacrylate, neopentylglycol diacrylate; acrylate esters of ethoxylated or propoxylated glycols and polyols, preferably propoxylated neopentyl glycol diacrylate and ethoxylated trimethylolpropane triacrylate; difunctional acrylates with a molecular weight greater than 200; and mixtures thereof.

5. The ink claimed in any one of the preceding claims, wherein the multifunctional acrylate monomer is present in an amount from 50 to 95% by weight, preferably from 60 to 80% by weight.

6. The ink claimed in any one of the preceding claims, wherein the vinyl ether monomer is selected from : diethylene glycol divinyl ether, 1,4-cyclohexanedimethanol divinyl ether, triethylene glycol divinyl ether, ethylene glycol monovinyl ether and 1,4-cyclohexanedimethanol divinyl ether.

7. The ink claimed in any one of the preceding claims, wherein the vinyl ether monomer is present from 1 to 20% by weight, preferably from 7 to 15%, provided that the ratio of multifunctional acrylate monomer to vinyl ether monomer lies between 5:1 and 15:1.

8. The ink claimed in any one of the preceding claims, wherein the photoinitiator is a free radical photoinitiator, preferably selected from: benzophenone, 1-hydroxycyclohexyl phenyl ketone, 2-benzyl-2-dimethylamino-(4-morpholinophenyl)butan-1-one, benzil dimethylketal, bis(2,6-dimethylbenzoyl)-2,4,4-trimethylpentylphosphine oxide or a mixture thereof.

9. The ink claimed in any one of the preceding claims, wherein the photoinitiator is present from 1 to 20% by weight, preferably from 4 to 10% by weight, of the ink.

10. The ink claimed in any one of the preceding claims, wherein the colouring agent is a dispersible pigment.

11. The ink claimed in claim 10, wherein the dispersible pigment is present from 0.5 to 12% by weight, more preferably from 1 to 5% by weight, of the ink.

12. A method of ink jet printing, wherein the method uses the ink claimed in any one of claims 1 to 11.

Application No: GB 0102227.6
Claims searched: 1-14

Examiner: Darren Handley
Date of search: 16 May 2001

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): C3V (VAL, VAM); C3P (PFEL)

Int Cl (Ed.7): C09D 11/00, 11/10

Other: Online: WPI, EPODOC, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB 2256874 A	(SERICOL) - see page 4, line 1- page 6, line 22 and example 1.	1-4, 6-14
X	GB 2255778 A	(SERICOL) - see page 3, line 8- page 5, line 28	1-14
X	GB 1414065 A	(BAYER) - see page 2, line 3- page 3, line 30	1-10, 12-14
X	US 5888649 A	(SERICOL) - see col. 3, lines 20-35, col. 4, lines 57-66, col. 6, lines 2-20, col. 11, lines 58-67, col. 12, lines 51-67 and col. 15, lines 18-20.	1-10, 12-14
X	JP 59179570 A	(MOROHOSHI) - see WPI abstract AN - 1985-076630 [25]	1-5, 7-14

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.